

PROJECT SQUID

TECHNICAL REPORT ARC-7-P

COMBUSTION STUDIES OF SINGLE ALUMINUM PARTICLES

by

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ATLANTIC RESEARCH CORPORATION

Alexandria, Virginia

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A COOPERATIVE PROGRAM
OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

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PROJECT SQUID HEADQUARTERS
JAMES FORRESTAL RESEARCH CENTER
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

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Combustion Studies of Single Aluminum Particles

(ABSTRACT)

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The problem of combustion of aluminum droplets differs from that of other, more volatile, fuels in several respects, the most important one being the formation of a condensed oxide product. The present work deals with the process of combustion of single particles which must be understood before studies of cooperative effects at higher pressures are undertaken.

The earlier work on combustion of single aluminum particles on a flat flame burner in presence of appreciable amounts of water (1) is briefly reviewed. This work gave several significant experimental and theoretical results. (a) The particles ignite only when their temperature reaches the melting point of alumina ($2303 \pm 20^\circ\text{K}$). This was shown to occur if the ambient temperature is at least $2200\text{--}2300^\circ\text{K}$. (b) The ignition delay time is proportional to the square of the particle diameter. (c) Combustion of particles involves formation of hollow alumina bubbles. (d) At high concentrations of ambient oxygen the burning particles undergo fragmentation.

The new experimental data were obtained by two different methods. The first one utilized hot gases formed on the flat flame burner, as in earlier work; the difference was that the product gas was virtually free of moisture (about 0.5 per cent). In the second method, spherical aluminum particles of controlled sizes were burned in the combustion products of ammonium perchlorate with organic fuels added to increase the temperature. While this technique is designed for studying the effect of pressure, results reported here were obtained primarily at one atm. The products of such flames contain large amounts of water and some hydrogen chloride. Adiabatic flame temperatures and detailed compositions of product gases both for the burner flames and solid fuel flames were computed by an IBM-704 program. In both cases, phenomena were followed photographically and by collection techniques.

Data on ignition of aluminum particles obtained from both methods are strikingly similar to the previously reported results (1). The minimum ignition temperatures are the same ($2200\text{--}2300^\circ\text{K}$) within the experimental error. The pre-ignition delays increase with the square of the particle diameter. The second method, which can be utilized also at elevated pressures, revealed that aluminum does not ignite in the products of pure ammonium perchlorate flames at any pressure up to 2000 psi. Since the temperatures involved are far below 2300°K , this result is reasonable.

On the other hand, once the particle has ignited, the results of its

combustion in the low-moisture gases are quite different from those reported previously. There is no evidence of formation of hollow oxide bubbles. Rather, the combustion is characterized by a steady diminution of the metal particle, and the oxide product consists of small particles. The amount of moisture necessary for appearance of large translucent bubbles is 5-10 per cent. Combustion of particles in low-moisture media is considerably more rapid. While time-exposure photographs of burning particles in high-moisture gases show sharp tracks, there is much diffuse luminosity in low-moisture media, indicating combustion of aluminum vapor.

All these observations point to the conclusion that the ignition process is not affected by the moisture content of the hot ambient gas. The pre-ignition reaction is always controlled by diffusion through the oxide layer which coats the particle, and ignition occurs only when the layer melts, regardless of the composition of ambient gas. On the other hand, there is a distinct effect of water vapor on combustion of aluminum particles. In the virtual absence of water, diffusion and combustion take place freely in the gas phase, whereas in the presence of significant amounts of water the process is impeded and confined to a smaller region, because the reactants must diffuse through a condensed oxide layer. Hence the qualitative and quantitative differences. The results of this work suggest a chemical alteration of some property of molten alumina by water, but a proper analysis of this effect must be deferred until more experimental detail of behavior of alumina in the presence of water is obtained.

Reference

1. Friedman, R. and A. Maček, Combustion and Flame 6, 9 (1962).

COMBUSTION STUDIES OF SINGLE ALUMINUM PARTICLES

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Description of the Problem

The general problem of droplet combustion is well known and an extensive literature exists. Burning aluminum droplets have properties, however, which make the previous body of work on other, generally more volatile, fuels almost irrelevant. Let us consider these properties.

Firstly, the combustion product, alumina, melts at 2303°K, and boils with decomposition at about 3800°K in the presence of one atm of the decomposition products (Al, AlO, Al₂O, Al₂O₂, O, O₂). Since there is insufficient combustion energy available to vaporize more than a fraction of the alumina formed, the maximum flame temperature will be governed by this pressure-dependent dissociative vaporization process. On the other hand, aluminum boils at about 2700°K at one atm. Thus, the phases in which reactants and products may exist in the combustion zone, as well as the possibility that a continuous molten oxide film may exist between fuel and oxidizer, become of dominant importance in determining the mechanism and rate of the process.

Secondly, the combination of very high flame temperature and high emissivity of a large or dense cloud of aluminum particles leads to such an intense radiant flux that this will become comparable with energy transfer by thermal conductivity through the gas during the combustion process. Accordingly, cooperative phenomena characteristic of a cloud of particles must be superimposed on single-particle characteristics for proper description of the process.

Thirdly, special factors enter when one becomes concerned with aluminum combustion under rocket motor conditions. The high pressures cause increases in the emissivity of the combustion products, the boiling point of aluminum, and the flame temperature. The oxidizing species may be water vapor and carbon dioxide rather than free oxygen. Halogen compounds may be present. In addition to these variables which may influence the ignition process and combustion rate, one must also be critically concerned with the particle size of the alumina formed, because of the effect on thermal and velocity lag in the nozzle expansion process.

The present research effort is based on the idea that single-particle combustion at atmospheric pressure should be thoroughly understood before the more difficult studies of cooperative effects at high pressures are undertaken.

Review of Past Work

Except for our earlier paper (1), no detailed account of aluminum particle combustion has appeared in the open literature. Cassel and Liebman (2) failed to obtain ignition of aluminum particles in a furnace at 1400°C. Gordon (3), Fassell et al. (4), and Wood (5), have briefly described experiments involving observations of particle ignition induced by injection into non-metallic flames. Fassell et al. (4) also describe hollow spheres of metal oxide which may be recovered in the combustion products.

In the following paragraphs, the highlights of our earlier work (1) are reviewed.

The plan has been to inject single spherical aluminum particles of controlled sizes (10 to 74 microns) into hot product gases of propane-oxygen-nitrogen flames and to observe ignition and combustion behavior. A previously described (1) flat-flame burner of 4.25-cm diameter, operating at atmospheric pressure, was employed to produce a uniform laminar flow of combustion products of known and independently variable temperature and oxygen content. (A substantial water vapor content, 14-18 per cent, was always present, a fact which will later be seen to be significant.) Combustion behavior of injected particles was studied both by photographic and particle-recovery techniques.

It was found that injected particles would only ignite under certain conditions. Investigation of critical conditions for ignition showed that particle size and ambient oxygen content were relatively unimportant variables, but an ambient gas temperature of about 2300°K was the necessary condition for ignition. This coincides with the melting point of aluminum oxide. A detailed mathematical theory of the ignition limit was developed (1) which assumes that melting of the protective oxide layer causes a discontinuous increase in the surface reaction rate, leading to ignition.

An ignition delay time was measured in those cases in which ignition occurred. This time, which was found to vary with the square of particle diameter, was in agreement with a theoretical calculation of its magnitude. The calculation was based on the particle being heated from its initial state to the alumina melting point by conductive transfer from the hotter ambient gas. It was shown that the Nusselt number may be taken as two and that radiation may be neglected under the prevailing experimental conditions. The agreement between measurement and calculation shows that oxidative heating is negligible during this pre-ignition period.

Studies of the combustion mechanism of the ignited particles revealed a number of unexpected phenomena. When the ambient gases contained less than 28-38 per cent oxygen (depending on ambient temperature), a burning particle would appear as a sharp, straight, vertical track on an exposed photographic film. This mode of combustion is associated with growth of transparent alumina bubbles. The particles frequently burn on only one side, and may rotate at several thousand revolutions per second. The burning time is roughly proportional to the 1.5 power of particle diameter.

We believe that in the above mode of burning the aluminum starts to boil soon after ignition and inflates the surrounding alumina bubble asymmetrically, the not-yet-burned metal adhering to one side of the bubble. The combustion occurs at the bubble, as aluminum vapor meets oxygen. The bubble is an important diffusion barrier to reaction.

At ambient oxygen content above 28-38 per cent, another phenomenon, fragmentation, was observed. Particulate matter may be ejected in a random direction from the burning droplet. This may be preceded by ejection of a diffuse cloud from the burning particle, the cloud presumably being aluminum vapor burning to form colloidal alumina. The occurrence of droplet shattering greatly reduces burning time.

We believe that the higher reaction rates and metal flame temperatures associated with the higher oxygen content lead to more rapid boiling of the aluminum (superheating is possibly but not necessarily involved), resulting in rupture of the alumina bubble.

In the new work to be reported below, which is still in progress, emphasis is being placed on study of the variables governing transition between various modes of combustion. Effects of composition of ambient atmosphere and pressure are being sought in particular.

Combustion in Moisture-Free Gases

The hot gases produced by the propane-oxygen-nitrogen flames utilized in the above-described work had a rather high water vapor content, typically about 18 per cent. In order to assess the significance of this variable, experiments have been conducted with dry carbon monoxide-oxygen-nitrogen flames, stabilized on the same burner. In order to obtain a stable flat flame, it has been necessary to add a small proportion of hydrogen to the mixture, so that about 0.5 per cent water vapor is now present in the combustion products.

As in previous work (1), the flame temperatures were computed by an IBM-704 program which assumes adiabatic equilibrium conditions, and takes into account all pertinent dissociation equilibria. Temperatures were then corrected for the heat loss to the water-cooled burner. Adiabatic temperatures for carbon monoxide flames are shown in Figure 1.

The following experimental results on combustion of aluminum particles in low-moisture gases are similar to the results in high-moisture media:

- a. Ignition is very abrupt at all ambient oxygen concentrations higher than about 2 per cent. The pre-ignition delays increase with the square of particle diameter as in the high-moisture gases.
- b. The most important requirement for ignition, by far, is that the metal particle be heated to the melting point of alumina ($2303 \pm 20^\circ\text{K}$). As has been shown in the previously developed theory (1),

this occurs at ambient temperatures between 2200 and 2300°K, depending on the amount of oxygen present. Figure 2 shows the minimum ignition temperatures as function of oxygen content for particles of 34-micron average diameter both in high-moisture and low-moisture media. It can be seen that the linear relationship holds down to about 2 per cent of ambient oxygen. The relatively wide scatter of the data at very low oxygen content is due to the fact that in such oxygen-poor gases the ignition criteria are ill-defined.

Combustion of aluminum particles in low-moisture differs from that in high-moisture media in the following aspects:

- a. While the striking feature of aluminum combustion in the presence of appreciable amounts of water vapor is the growth of a hollow shell of aluminum oxide attached to the unconsumed portion of the metal particle, the completely burned particle being a hollow sphere of translucent aluminum oxide of approximately the same size as the original aluminum, there is no evidence of such a process in low-moisture gases. Rather, the combustion is characterized by a steady diminution of the original particle; the oxide product consists of particles of irregular shapes and widely varying sizes smaller than the original particle. If, however, a significant amount of hydrogen is added to the carbon monoxide flame, the large translucent bubbles reappear. The amount of hydrogen necessary for this result is 5 to 10 per cent.
- b. Combustion of aluminum particles is considerably more rapid in low-moisture media than in the presence of appreciable amounts of water vapor. This can be seen from Table I which gives experimental pre-ignition and combustion times for two particle sizes in two atmospheres which are similar except for widely different moisture contents.
- c. While typical time-exposure photographs of burning particles in high-moisture gases show sharp tracks, there is much more diffuse luminosity in the low-moisture gases. This is illustrated by Figure 3 and 4 which show photographs, taken at 1/50 sec, of burning particles in low-moisture and high-moisture media; the oxygen content in both cases is quite high. In the case of the high-moisture ambient gas, the tracks are sharp both before and after fragmentation which occurs after about 2 msec. of burning. In the case of the low-moisture gas, large amounts of aluminum vapor appear adjacent to the particle. This appearance is often accompanied by sudden change in the direction of motion of the particle.

Combustion in Ammonium Perchlorate-Fuel Flames

While burning of aluminum particles on the flat-flame burner has given good results at atmospheric pressure, the method cannot be easily extended to higher pressures. A procedure is, therefore, being developed wherein aluminum particles are burned in the combustion products of ammonium perchlorate with fuels added.

Combustion can take place either in the open or in a window bomb at pressures up to 2000 psi. Small amounts of spherical aluminum powder of controlled sizes are admixed to the combustible mixture, and burned either pressed into strands or in loosely tamped powder form. The latter method, employed by Arden, Powling and Smith (6), appears somewhat more satisfactory. Our procedure has been to mix 0.05 or 0.1 per cent of aluminum powder of controlled size with a finely ground ammonium perchlorate-powdered organic fuel mixture which is tamped into cylindrical form (6.5 mm diam) surrounded by an annular "guard ring" of unaluminized perchlorate-fuel mixture of 17 mm diameter. Both trioxymethylene and plastisol-type polyvinyl chloride have been employed as fuels. The use of powdered fuels in a tamped or pressed composition rather than a polymeric binder system permits much greater latitude in fuel-oxidizer ratios and fuel type to obtain desired flame temperatures and combustion product compositions. Figure 5 shows calculated adiabatic flame temperatures as a function of pressure for the ammonium perchlorate-trioxymethylene system.

Experiments done so far have given the following results:

- (a) Aluminum does not ignite in the products of pure ammonium perchlorate flames at any pressure up to 2000 psi. In view of the fact that temperatures in such flames are far below the melting point of alumina, this result is most reasonable.
- (b) Aluminum particles do ignite in mixtures which contain sufficient amounts of fuel both at atmospheric and at higher pressures. The minimum ambient temperature necessary for ignition at one atm is 2250-2300°K, in excellent agreement with the results obtained in the gas-burner work.
- (c) The ambient gases in these experiments generally contain about 40 per cent water vapor, and the combustion process follows the general pattern previously established for high-moisture media. The particle tracks in photographs are sharp. Combustion products have been collected at atmospheric pressure, and were found to contain translucent oxide bubbles. The particles fragment if there is sufficient oxygen in the hot ambient gases. Figure 6 shows two pressed strands of mixtures of ammonium perchlorate and polyvinyl chloride, one without aluminum, the other containing 0.1 per cent of aluminum powder, burning at atmospheric pressure; the product gas contains very little oxygen. Figure 7 illustrates the process of fragmentation as it occurs at atmospheric pressure in the flame products of a loose powder mixture of ammonium perchlorate and trioxymethylene. In view of the fact that the combustion gas in Figure 7 contained only about 9 per cent of free oxygen, it appears probable that the fragmentation occurred upon contact with ambient air.

Discussion

The main topic requiring discussion is the pronounced difference in burning

characteristics induced by the presence of water vapor in the combustion atmosphere. The discussion of this problem must be highly speculative, because very little is known of the alumina-water interaction at flame temperatures.

Brewer and Searcy (7) heated molten alumina in a Knudsen effusion cell and found the rate of volatilization to be the same in the presence and absence of one micron pressure of hydrogen. They presumed from this that no very stable gaseous aluminum subhydroxide species, such as $AlOH$ or $HA1O_2$, exists. Also, Glemser and Volz (8), studying volatility of solid alumina at $1700^{\circ}C$, found no significant change when one atm of water vapor was present. However, R. F. Walker et al. (9) have reported qualitative experiments with the solar furnace which indicate the volatility of molten alumina to be considerably enhanced by a pressure of 25 mm water vapor. They are continuing the study of this interaction.

It is clear that more definitive experiments of behavior of molten alumina in the presence of water vapor must be carried out before our combustion results can be properly analyzed. However, we tentatively suggest at this time that our results are indicative of a chemical alteration of some property of molten alumina by water. For example, if a subhydroxide forms which is soluble in the molten alumina and changes its surface tension, or alternately forms early in the combustion process and decomposes again when the temperature has risen to a higher level, the bubble-forming property of the alumina to create a diffusion barrier to reaction could be influenced.

Summary

All experimental observations point to the conclusion that the ignition process is not affected by the moisture content of the hot ambient gas. The pre-ignition reaction is always controlled by diffusion through the oxide layer which coats the particle, and ignition occurs only when the layer melts, regardless of the composition of ambient gas. On the other hand, there is a distinct effect of water vapor on combustion of aluminum particles. In virtual absence of water, diffusion and combustion take place freely in the gas phase, whereas in the presence of significant amounts of water the process is impeded and confined to a smaller region, because the reactants must diffuse through a condensed oxide layer. Hence the qualitative and quantitative differences.

Acknowledgements

The authors wish to thank Mr. J. M. Semple for valued experimental assistance in this work. The work was sponsored by Project SQUID which is supported by the Office of Naval Research, Department of the Navy, under Contract Nonr 1858(25) NR-098-038. Reproduction in full or in part is permitted for any purpose of the United States Government.

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Table I
Some Ignition and Combustion Times

| Avg. Particle Diameter (microns) | Ambient Temp. (°K) | Percent O ₂ | Percent H ₂ O | Ignition Time (t _i , msec) | Burning Time (t _b , msec) | t _b / |
|--|--------------------------|------------------------|--------------------------|--|---|------------------|
| 35 | 2510 | 5.8 | 18.1 | 7.6 ± 0.4 | 10.5 ± 0.5 | 1. |
| 49 | 2510 | 5.8 | 18.1 | 11.7 ± 0.7 | ≈ 19 | 1. |
| 35 | 2510 | 7.9 | 0.5 | 10.7 ± 1.0 | 6.6 ± 0.7 | 0. |
| 49 | 2510 | 7.9 | 0.5 | 16.5 | ≈ 12 | 0. |

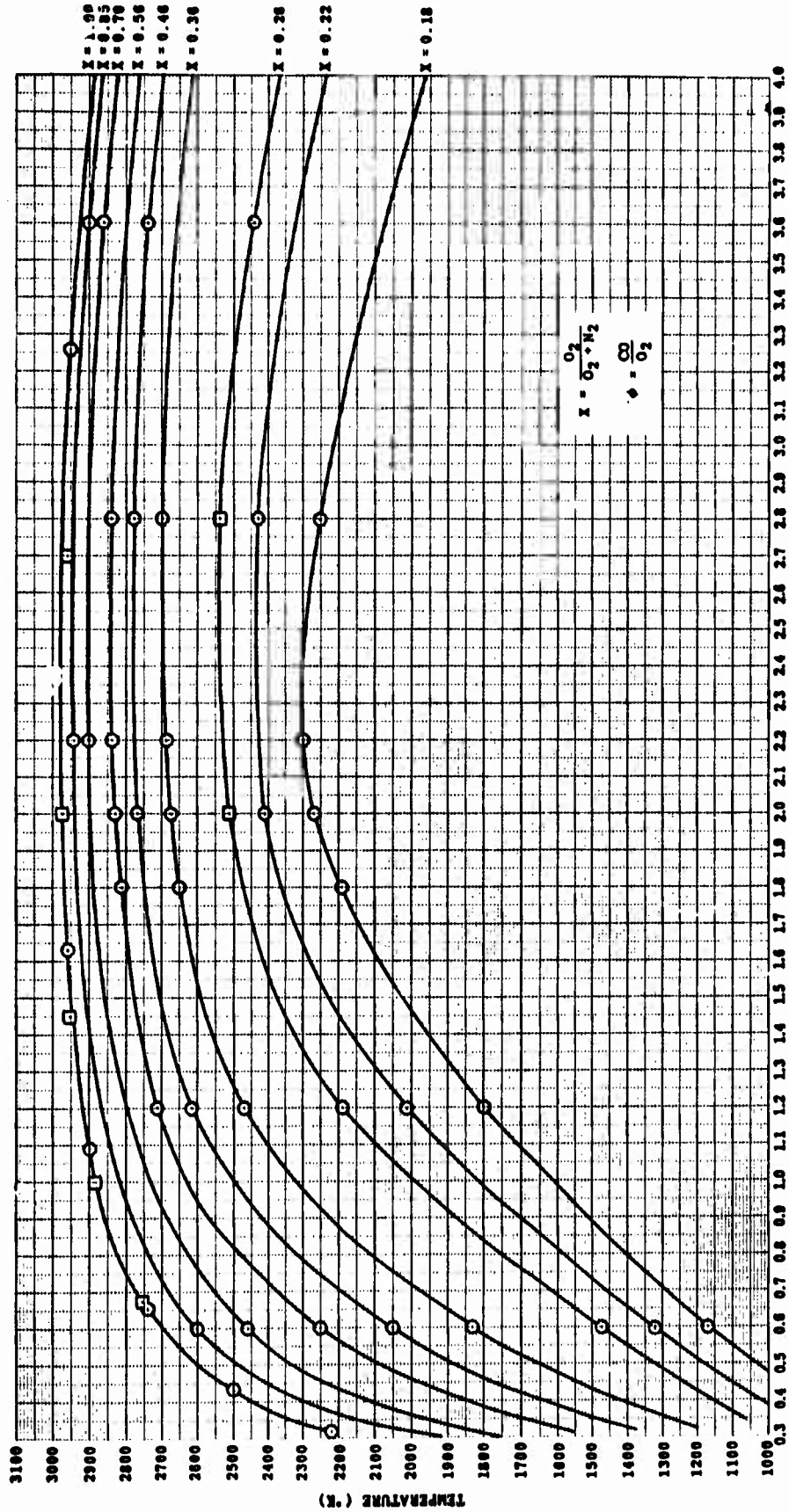


Figure 1. CALCULATED ADIABATIC FLAME TEMPERATURES OF CO - O₂ - N₂ MIXTURES AT ONE ATMOSPHERE.

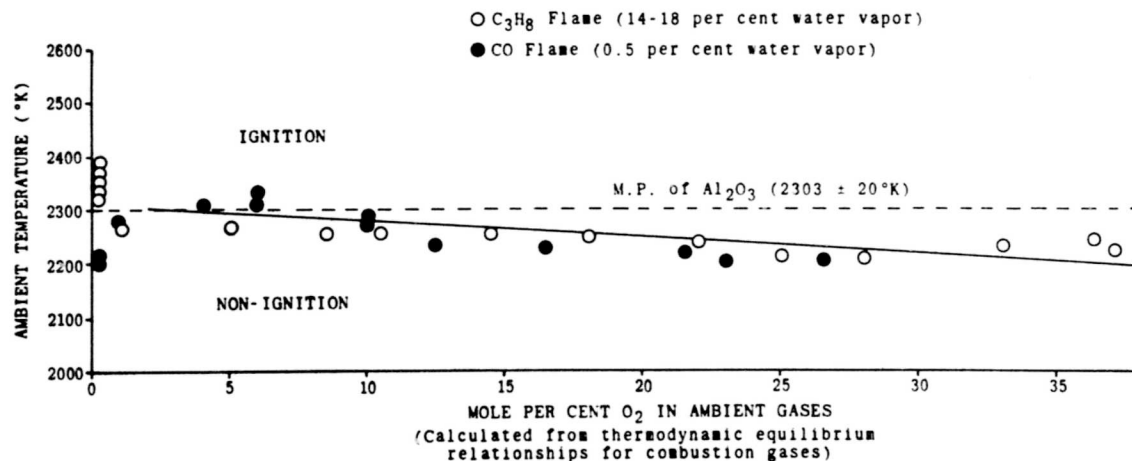


Figure 2. Minimum Ambient Temperature for Ignition of Aluminum Particles (Average particle diameter = 34 microns)

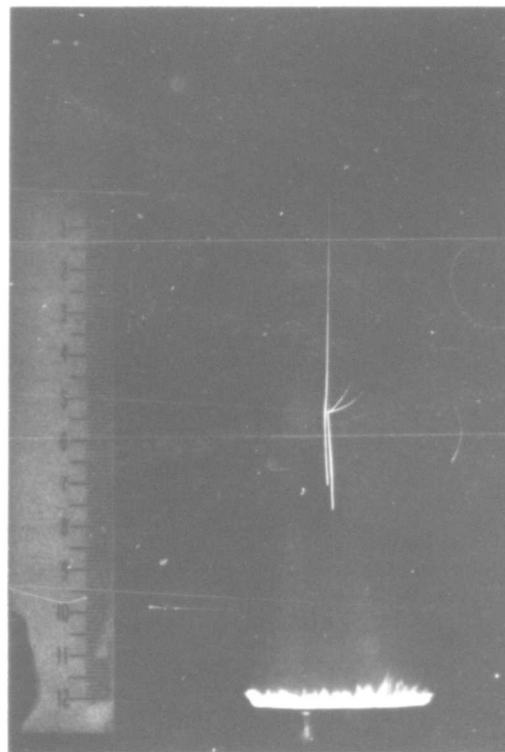


Figure 3. Burning and Fragmentation of 34-Micron Diameter Particles. Ambient Conditions: T = 2390° K, O₂ = 31.2%, H₂O = 17.0%. The Scale is in Centimeters.

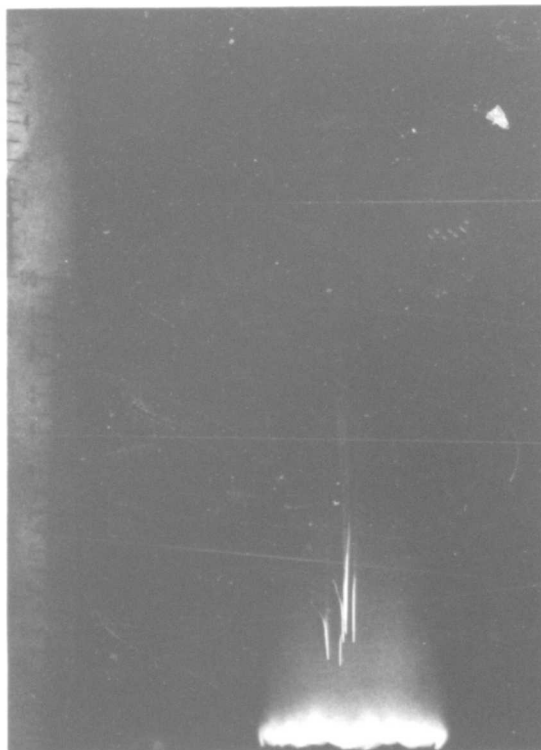


Figure 4. Burning of 34-Micron Diameter Particles.
Ambient Conditions: $T = 2580^{\circ}\text{K}$,
 $\text{O}_2 = 34\%$, $\text{H}_2\text{O} = 0.5\%$.

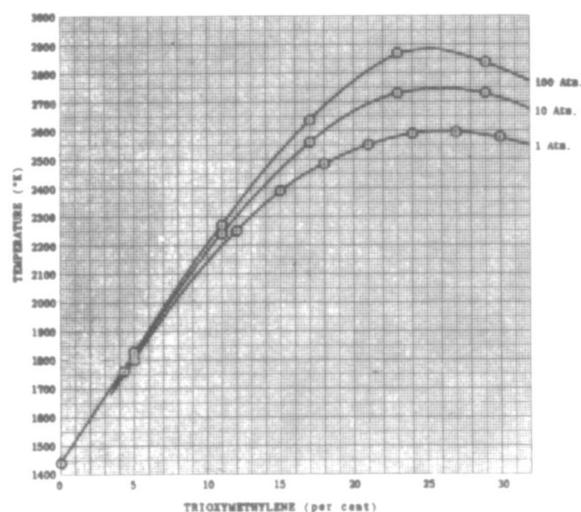


Figure 5. Calculated Adiabatic Flame Temperatures
of Ammonium Perchlorate - Trioxymethylene
Mixtures at Several Pressures.

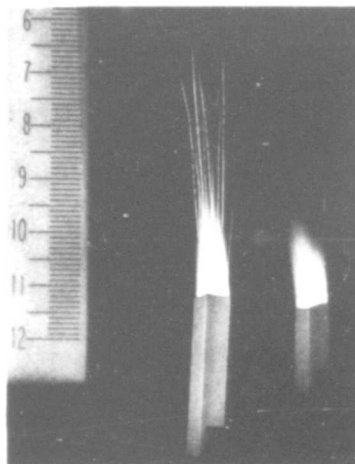


Figure 6. Burning of Pressed Strands Containing 78.7% Ammonium Perchlorate and 21.2% Polyvinylchloride. Left: 0.1% Aluminum (34-micron diameter) Added. Right: No Aluminum. The Scale is in Centimeters.

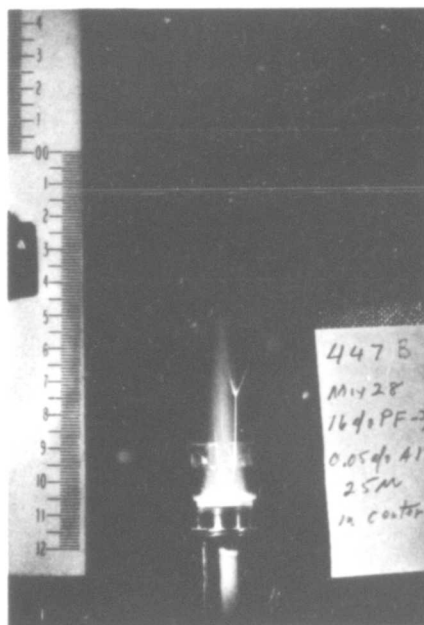


Figure 7. Burning of a Loose Powder Containing 84% Ammonium Perchlorate and 16% Trioxymethylene; 0.05% Aluminum (25-micron diameter) Added. Ambient Conditions: $T = 2410^{\circ}\text{K}$, $\text{O}_2 = 9.2\%$, $\text{H}_2\text{O} = 43.2\%$. The Scale is in Centimeters.